Effect of H$^+$ Ion Activity and Ca^{2+} on the Toxicity of Metals in the Environment

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The role of acidity in determining and restricting plant distribution and performance is discussed. In soils especially, a key effect of H$^+$ ion concentration is on the solubility of potentially toxic heavy metals such as aluminum, manganese, zinc, iron, copper, and nickel. Al has been reported from many studies since the 1920's as the key determining toxic factor in acid soils. Some acid-tolerant species have been shown to be especially tolerant of Al, and mechanisms of tolerance have been suggested. Mn is also a commonly toxic factor at soil pH less than 5.0. Calcium has been shown to alleviate Mn toxicity. Low pH soils are also generally low in Ca, K, Na, and P; all essential major elements for plant growth. In lakes and marine situations acidic waters are uncommon as the waters are buffered. Calcium is again ameliorative of metal toxicities. The pH, redox, and valency state are critical in determining nutrient availability and metal speciation. Recent increases in the H$^+$ ion content of precipitation have caused increased acidities of freshwater lakes in Scandinavia and eastern North America, which have depleted biota, including fish populations.

Introduction

The importance of soil acidity to crop growth has long been recognized. Acidic soils are known to have nutrient problems, both of toxicity and deficiency, and the empirical agricultural response to this has been to lime them, so that the soil pH falls in the range of 5.0 to 7.5. Acidic ecosystems, such as bogs and peat wetlands, are also known to have distinctive plant communities and to be generally unproductive. Irrespective of soil acidity, plant nutrients have to be taken up from solution, so that the solubility of a particular element or compound is a key consideration in soil fertility. H$^+$ ion concentrations play a determinant role in the solubility of compounds both in soil and in aquatic systems. In freshwater systems, also, the nutrient supply for plants must be in soluble form. The buffering capacity of the waters, in turn, will be critical in determining the response of the water body to H$^+$ ion inputs. Sea water is especially well buffered. Sillen (*1*) has suggested that the oceans are the result of a gigantic acid-base titration in which acids, which have leached out of the interior of the earth, are titrated with bases that have been set free by the weathering of primary rock. In like manner, one can

consider that the soil solution is a concentrated form of buffered lake water. Only in soils with a very low cation exchange capacity—such as those derived from sand—is there a poorly buffered soil equivalent of the nutrient-poor, oligotrophic lake waters developed on recently glaciated granitic and Shield rocks in Scandinavia and northern America.

Heavy metals at low pH, i.e., < 5.0, are largely soluble and therefore available to be taken up by plants and to exert potential toxic effects. In soils aluminum, manganese, iron, copper, nickel, and zinc fall into this category so that acid soils (or lakes) at these pH values have present in or on them species which are tolerant of these stresses. Changes which may occur and which increase the H$^+$ ion activity will increase the heavy metal and ionic stresses, leading to species changes favoring more tolerant organisms. It is also a commonly observed phenomenon that acidic environments are nutrient poor, with such key elements as phosphorus and nitrogen being at a shortage.

Plant species, including fungal and bacterial microbial populations, show characteristic occurrences, with a basic pattern of pH ranges. The distribution of many native species is confined to either calcareous (high pH) soils or acidic soils. Calcareous floras are typically rich in species while acidic ones are species-poor. Despite this, some species cover a wide range of soil pH (3.5-7.5) but

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studies (2-4) have very frequently revealed that they are composed of populations adapted to specific, more limited ranges of pH, although pH *per se* is generally not the major causal factor.

Changes in the pH of many lakes have been reported in recent years as a result of acid precipitation caused by long distance dispersal of polluted air masses from industrial centers. This has been especially true of Scandinavian lakes. Poorly buffered systems are especially vulnerable. The effects have often been profound, with changes in both flora and fauna of the affected lakes. Fish populations have declined or become extinct (5).

The total quantity of a metal in the environment, i.e., in water or soil, is only one facet of its impact. If it is to exert any biological influence it has to be present in an available form. The chemical form of occurrence in the soil/water, and the presence of interacting complexing agents, the possible adsorption of the metal onto colloids, clays etc., metal-metal interactions and competitive uptake, the co-precipitation with other more common elements, etc., are all important in determining the specific impact. In the following, the effect of acidic or acidifying environments on plants is discussed, with special attention being given to calcium interactions.

Acid Soils

pH and Heavy Metal Toxicity

In a review of acid soil effects, Hewitt (6) listed the following: direct injury by H^+ ions; indirect effect by: impaired absorption of Ca, Mg, and P, by increased solubility and toxicity of Al, Mn, and Fe, and reduced availability of P by aluminum precipitation of phosphorus; reduced availability of Mo; low base status as a result of Ca deficiency and reduction in Mg and K uptake; abnormal biotic factors (impaired nitrogen cycle and fixation, impaired mycorrhizal activity, attack by pathogens); and accumulation of soil organic acids.

Over the past 70 years, a large number of workers have established the importance of free aluminum ions as toxic factors in soils with a pH below 5.0. Hartwell and Pember (7) described aluminum toxicity in barley, while Ligon and Pierre (8) described a low pH induced phosphorus deficiency. In agricultural soils, aeration was found to be important for toxicity. In high sulfur soils, well aerated soils showed increasing acidity as a result of sulfide oxidation to sulfate. Rorison (9) recalculated data from Sparling (10), from which he suggested that in soils with a pH < 3.0 iron exists almost exclusively as ferric ion which is highly toxic, but in soils with pH

3.0-5.0, highly soluble aluminum is the key limiting factor. Ferrous ion is not a toxic growth-limiting factor, even though it is the predominant iron form in soils with a pH greater than 3.0.

Aluminum and other polyvalent cations inhibit calcium uptake, and also form insoluble salts with phosphate. Clarkson and Sanderson (11) found that labeled scandium, ^{46}Sc, behaved chemically very similarly to aluminum, for which isotopes suitable for experimentation do not exist. In onion they found that ^{46}Sc very rapidly penetrated meristematic cells, but migrated slowly across plant secondary walls. They also found that aluminum, scandium, and iron inhibited the uptake of calcium from culture solutions at pH 4.0-4.2. Each polyvalent ion reduced the amount of calcium in waterfree space and in the Donnan free space but had no effect on the nonexchangeable calcium. Since calcium is an integral part of the cell membrane structure, Woolhouse's (12) report that leakage of K occurred from the root tips of acid soil-susceptible plants following high aluminum treatment is consistent with membrane disruption. It has similarities to hemocyte leakage of K.

The influence of H^+ and Ca^{2+} ion concentrations, separately and together, on the patterns of uptake and distribution of copper has been studied by Mierle and Stokes (13) in the green alga *Scenedesmus* in a strain isolated from a copper-contaminated lake and in a laboratory strain. The presence of calcium or of a high H^+ ion concentration was found to reduce markedly the speed at which copper entered into the cells by diffusion across the semipermeable membrane, i.e., the plasmalemma. The authors speculated that calcium reduced the electrostatic forces of the negatively charged groups in the membrane. A second, fast component of uptake appeared to involve binding to the cell wall and was not influenced by Ca^{2+} ion but was influenced by pH. This probably reflects competition by H^+ ions for negatively charged binding sites. Polyvalent cations and pH have been observed to have a somewhat similar influence on the selective permeability of epithelial cells to monovalent ions such as K^+ (14).

In laboratory and field experiments Rorison (15) showed that species differed markedly both in their calcium requirements and in their aluminum sensitivity. The acid-tolerant rush *Juncus squarrosus* had a requirement, in solution culture, of 10 mg Ca/l., while the acid-sensitive species *Scabiosa columbaria* required 400 mg/l. for optimal growth. Snaydon and Bradshaw (3) found populations of the grass *Festuca ovina* obtained from a low calcium and a high calcium soil to differ in their ability to extract calcium from a soil at pH 4.0. The low cal-

cium soil populations had an enhanced ability to remove calcium when its supply was low. Wide differences between species in the ability to extract calcium from soil have also been found for other grasses as well as for legumes [16].

Jackson [17] reviewed the literature on aluminum, manganese, and acid soil toxicity. He emphasized the importance of both these metals and their dependence on H^+ ion concentration in exerting their influence. He also noted that calcium ameliorated manganese toxicity. Sutton and Hallsworth [18] found that calcium additions were able to alleviate manganese toxicity at a pH of 4.0 in tomato.

The effect of microorganisms in soil in changing the microclimate of the roots was shown by Boswell [19], who studied nitrifying organisms in a soil of pH 4.0. When fed with ammonium fertilizer, at pH 6.0 apple trees developed a pH gradient of 4.0 to 4.5 immediately adjacent to their roots, while when fed with nitrates at pH 4.5 they developed an acidity at their root surface of 5.6.

Certainly microorganisms proximal to root systems influence the availability and uptake of elements. Nitrifying bacteria, such as *Nitrobacter* and *Nitrosomonas*, show lower populations in acid soils, and at pH 4.0, fungi rather than bacteria predominate. At pH 3.0, very few soil organisms are able to survive. The high calcium requirements of nitrifiers may be a factor in this.

Acid Precipitation: Effects on Soils

Leaching of bases in acidic soils or soils subject to acid rain is very important, with Ca and Mg being lost in large amounts. In Norwegian studies Abrahamsen, Horntvedt, and Tveite [20] simulated acid precipitation with 50 mm/month of rainwater at pH 3.0 (acidified with H_2SO_4). A significant leaching of calcium and magnesium occurred, with a decrease in the base saturation of humus. Norton [21] predicted potential solubilization of aluminum, manganese and iron from clay minerals by exchange with H^+ at pH below 4.0 and rapid loss of Al^{3+} below pH 3.0. In our own work in the heavily sulfur-fumigated smelter area at Sudbury, Ontario, we have found structural changes in humic acids in soils at or below pH 3.0 in which substitution of sulfonic acid groupings for carboxylic acid groupings appears to have taken place. The metal binding capacity of these humates has been altered [22]. Al^{3+} was also found in runoff from these soils, as well as in soils from a naturally-fumigated area in the western Canadian arctic. Abrahamsen, Horntvedt, and Tveite [20] found that rain acidified to pH 2.0 caused leaching of about 85% of Al^{3+} by

replacement. They also reported that the leaching of divalent cations (Ca, Mg, Mn) was much greater than that of monovalent cations (Na, K). Whitby and Hutchinson [23] found that in contaminated soils, nickel and copper were directly toxic to seedling growth at soil pH's of less than 4.0, while liming of these soils largely eliminated this toxicity. Dahl and Skre [24], Overrein [25], and Tamm [26] concluded from tree growth ring analysis that in Scandinavia very little evidence of an effect of acid precipitation exists for forests, while Malmer [27] suggested that such an effect may not appear until forest clearance takes place, with loss of soluble nitrates to the watershed.

Aquatic Systems: Acidification Effects

The increasing acidification of lake and river waters in areas subject to rain and snowfall from air masses travelling from industrially polluted areas has been referred to previously. These air masses often contain a high concentration of S compounds, which form strong acids and N, which does the same. They also characteristically are metal polluted. The influx of large quantities of H^+ ions into poorly buffered systems can cause quite severe effects. In 20 years or so the pH of many affected lakes in Norway and Sweden have dropped 2 or 3 pH units, representing an increase in H^+ ion concentration of 100- to 1000-fold [28]. The soils washed by this acidity are subject to leaching. Wright et al. [28] studied the water chemistry of 155 Norwegian lakes and calculated inputs and outputs of elements. They found an excess of sulfate compared with the coastal input. Where the bedrock of the lakes was carbonate, the pH of the lakes was > 6.5 irrespective of inputs, i.e., they were well buffered. Acid lakes showed elevated levels of SO_4^{2-}, Ca^{2+}, Mg^{2+}, and Al^{3+}. Using Cl^- as a marker element for saline contributions, they found about 90% of the sodium and magnesium in wet precipitation attributable to seawater salts, and only 25% of the calcium and potassium so attributable. Accumulation of aluminum in the lakes was not from precipitation directly, but from soil leaching. Watershed studies confirmed the loss of calcium and magnesium from the system. Hutchinson has similar data for acidic ponds and lakes in Canada, with leaching of manganese and aluminum from acid soils.

Many biological changes have been reported, including changes in phytoplankton and zooplankton populations, where a pH < 5.0 appears to be critical. Aquatic macrophyte floras have changed, with a notable spread of the aquatic moss *Sphagnum* in

shallow waters (29). Fungal mats now cover shallow lake bottoms. Insect populations have declined, with the emerging stage of adults being especially vulnerable, since they come to the surface in spring when the early meltwater of polluted snow enters the lakes. This early meltwater is especially high in H^+ ions and has a deleterious effect on the emergent insects.

The spawning and reproductive stages of fish also are vulnerable, with aging populations of large fish occurring in lakes prior to population extinction. Low serum calcium concentrations during the period of ovarian maturation have been implicated in this reproductive failure of fish (30).

Reduced phytoplankton populations, especially of Chlorophyceae and Cyanophyceae, have been found (31–33). Blue-greens are quite rare in acidic situations. The main effect found in comparing a number of lakes (31) was the overall reduction in species number. The benthic and periphyton algae became more dominant as the Sphagnum mats advanced. There were few species involved, notably Batrachospermum and Mougeotia. In acidified streams Dinobryon, Tabellaria and Binuclearia became dominant. In comparing the Swedish and Canadian situations, the similarities were remarkable (31, 32).

Zooplankton populations also declined, especially below pH 5.5. The important crustacean Gammarus lacustris was not found in Swedish lakes with a pH less than 6.0 (31). Adults could not tolerate exposure to waters of pH 5.5 for over 24–48 hr. This has effects on fish in addition to the loss of reproductive vigor noted above. Similar data have been reported from Norway (28).

Speciation, Complexation, and Redox Effects

Many factors influence the toxicity of heavy metals in solution as the H^+ ion concentration changes. The metal concentration and the metal species present are two key factors. Toxicity is also affected by alteration in equilibria, effects of H^+ on the ligand, and effect on the redox state of the heavy metal ion. Calcium is also influenced by these factors. At low pH the dissolution of carbonates is favored, while at high pH that of the bicarbonate ion is favored.

It has been shown (34) that in seawater, lead is largely associated with CO_3^{2-} and to a lesser extent Cl^- over the pH range 7–9. The four metals cadmium, zinc, copper, and lead were found to be complexed to a large extent in seawater. The percentage of the species present varied greatly with pH, except for cadmium. Differences were of a specific nature, with copper interacting primarily

with OH^- and CO_3^{2-} ligands, Zn^{2+} with OH^-, Pb^{2+} with CO_3^{2-} and Cl^-, and Cd^{2+} with Cl^-. Zinc underwent less complexation than cadmium, lead, or copper, and 17% remained uncomplexed at pH 8.1. Cadmium differed from the others in that it occurred largely associated with chloride ions over a pH range from 7.0 to 9.0 All the predominant forms were soluble so that there is no adsorption or precipitation.

Sibley and Morgan (33) compared the distribution of heavy metals in fresh and seawater. At pH 8.0 no ions of the 11 metals studied are absorbed in seawater, while in fresh water, all metals except cadmium have absorbed species, and for some, this represents a significant proportion of the total metal in the system (Figs. 1 and 2). About 50% of copper, nickel, mercury, silver, and chromium are adsorbed onto surfaces of inorganic precipitates, while less than 10% of cobalt, lead, and zinc are so adsorbed. In fresh water only zinc, nickel, cobalt, and silver are to any extent speciated as the free ion. Nickel is also speciated in free ionic form in seawater (Fig. 3).
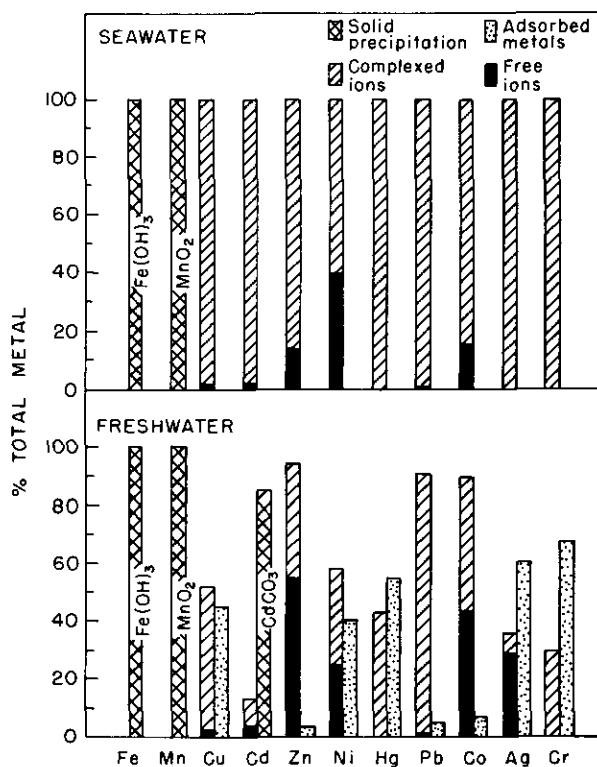

Figure 1. Distribution of dissolved and particulate forms of eleven trace metals in freshwater and seawater models. Dissolved forms include free ion and complexes; particulate forms include adsorbed metals and solid precipitates. Chemical composition of solid phases, e.g. Fe(OH)₃, is also indicated. Data of Sibley and Morgan (33).
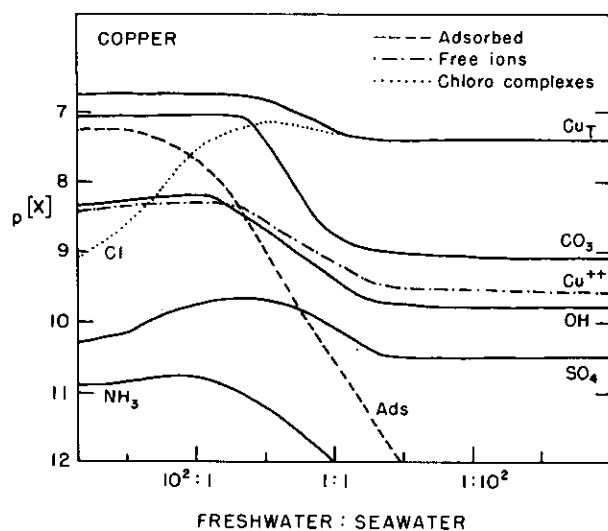
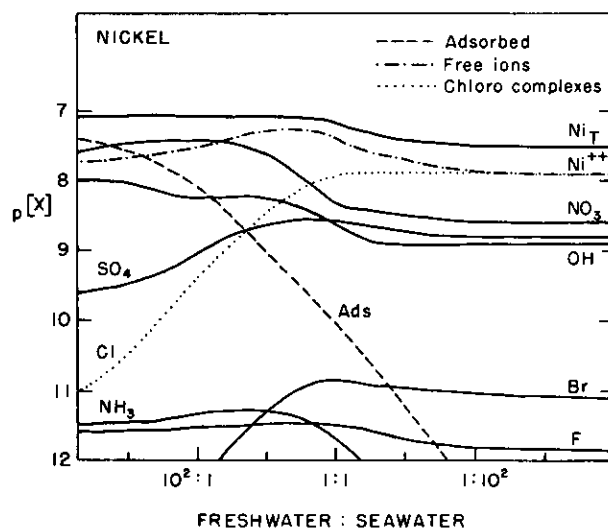FIGURE 2. Speciation of copper in various freshwater:seawater mixtures. Data of Sibley and Morgan (33).

FIGURE 3. Speciation of nickel in various freshwater:seawater mixtures. Data of Sibley and Morgan (33).

This increases its potential for toxicity, which in soil is increased at pH's below 5.0.

The redox potential of the plant surface and the environment, e.g., soil, sediment, are of considerable importance in determining both form and availability of a metal. For example, with Cd^{2+}, under anaerobic conditions (the redox potential E_H small or negative), at low pH the formation of CdS is possible, while at high pH, the formation of $CdCO_3$, is possible since CdS is insoluble. Under oxidizing (aerobic) conditions, the pH determines the occurrence of either Cd^{2+} or $CdCO_3$ forms only.

Stumm and Morgan (34) summarized the major features of pH/redox/valency effects for iron and manganese by means of a chart. Their use of models has proved invaluable in focusing on speciation in natural waters. In fresh water lakes, manganese is enriched in the hypolimnion in productive lakes, while the surface layers contain much less manganese. This enrichment cycle probably results from several steps, including a pH decrease shifting the equilibrium for adsorption exchange to favor desorption from MnO_2 and Fe_2O_3 colloids and reduction of Fe_2O_3 to ferrous oxides resulting in loss of adsorption exchange sites for Mn and subsequent release of Mn^{+2}. At high O_2 concentrations the ferric and Mn^{+4} oxide colloids have net negative charges, while at low O_2 the charges on the colloids are reduced. At high pH (7-9) the oxidizability of these colloids is favored, while at low pH (5-7) reduction is favored.

The role of organic ligands, especially humic substances, in affecting heavy metal availability is receiving a great deal of attention. It has been studied extensively, especially in soils by Schnitzer (35) and more recently in water by Gjessing (36). Humic acids complex many metals according to the Irving-Williams series $M^{+3} > M^{+2} > M^{+1}$. Within the divalent cation series, the charge/radius parameters and size of hydrated ion decide, for the most part, relative affinities for heavy metals. They function in soils and water. Experiments on the complexing capacity of waters and their ability to support algal growth in the presence of known potentially toxic quantities of copper have been performed (37, 38). When the complexing capacity is exceeded by the metal concentration, the lake waters became toxic as a result of free ions. Calcium additions play an ameliorative role, presumably by competition for binding sites. In an interesting contrast, Haghiri (39) showed that the toxicity of clay soils containing cadmium was increased by saturating the clay with Ca^{2+}. Two explanations are possible: (a) that Ca^{2+} treatment made more Cd^{+2} available for plant uptake by displacement or (b) that Ca^{2+} treatment stimulated Cd^{2+} uptake. While Ca^{2+} may overwhelm the available sites for clay binding, with humic substances the series of successive sorption suggests it must affect the plant more directly, i.e., Cu > Pb > Cd > Sr > Ca.

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